

KINETICS OF THE FORMATION OF SUBSTITUTED DIAMIDES  
OF CARBONIC ACID.

By  
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Being a thesis submitted for the degree of

DOCTOR OF PHILOSOPHY

in the Faculty of Science,

University of Tasmania.

AUGUST

1952.

MEMORANDUM.

This project came into being as a result of earlier work carried out in the Department of Chemistry, University of Sydney, in 1946. The original project at Sydney was a kinetic study of the urea-formaldehyde reaction and the results were incorporated in a thesis for the degree of Master of Science (Syd.), later published in J. Phys. Colloid Chem.

In 1944-45 the author was associated with a newly established factory for the production of phenoplastics and aminoplastics. As Research Chemist, Beetle-Elliott Plastics Pty. Ltd., he was given the task of carrying out the developmental work necessary for the establishment of the first plant for the manufacture of urea-formaldehyde condensation products in Australia.

Early in this work it was realised that notwithstanding formulae and manufacturing data supplied by the parent Beetle Company in England, the use of Australian raw materials introduced many difficulties which were not easily reconciled with existing knowledge of the reaction.

Despite a history of over sixty years and intensive research by many workers there was and still is, incomplete understanding of the complex condensation between urea and formaldehyde which is the basis for the production of many important technical plastics exemplified by Beetle, Plaskon, Scarab, Uformite and others.

Accurate quantitative data concerning more particularly the initial condensation, was not readily available in the literature and a high proportion of the information was of a

rather vague nature contained in patents.

Prior to 1946 no work had been published on the kinetics of the urea-formaldehyde reaction and the Sydney project was undertaken with a view to examining the initial condensation and reaction mechanism. Owing to other employment during the period 1946-48 it was not found possible to continue with this project even though some interesting points had been raised which required further examination.

In 1948 workers in the United States and Sweden published several papers on the kinetics of this reaction and at present the work still continues mainly in the United States, Australia, Sweden and Belgium.

When the opportunity arose in 1949 for further work on this subject and due to the interesting papers which had appeared in the intervening years, the author sought approval of this project as work for the Ph.D. degree.

This thesis is composed essentially of four papers published (or in press) in the Journal of the American Chemical Society. The work was published as results came to hand since as similar projects had been commenced in other countries, any great delay in publication might have resulted in some duplication of work. In the case of the author, the delay in publication would have been some four years as the project was undertaken on a half-time basis owing to teaching duties in the Department of Chemistry, University of Tasmania. The normal time spent on research by Ph.D. candidates in the University of Tasmania, is two years full-time work.

iv.

For the convenience of examiners a supplement (separate from this thesis and not for examination) is attached. This supplement contains the more important papers on the kinetics of the urea-formaldehyde reaction published between 1947-52 and which may be required for reference.

## ACKNOWLEDGEMENTS.

I wish to express my appreciation for the advice and assistance of the following:

Professor E.E. Kurth, Professor of Chemistry, University of Tasmania; Dr. T. Iredale, Reader in Physical Chemistry, University of Sydney; Dr. J.B. Polya, Senior Lecturer in Organic Chemistry, University of Tasmania; Dr. G.A. Crowe, Bakelite Company, Union Carbide and Carbon Corp., Bound Brook, New Jersey, U.S.A.; Dr. I.R. Bick, Lecturer in Organic Chemistry, University of Tasmania; Dr. J.S. Fitzgerald, Division of Industrial Chemistry, Commonwealth Sci. Ind. Res. Organisation, Melbourne; Beetle-Elliott Plastics Pty. Ltd.; University of Tasmania; Research Grant, Commonwealth of Australia.

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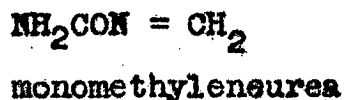
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## INTRODUCTION.

A serious drawback which hindered the elucidation of many reaction mechanisms in organic chemistry, was the lack of accurate quantitative data. The classical investigation by Lapworth<sup>1</sup> of the halogenation of ketones initiated a new kinetic era in organic chemistry promoting the search for more exact knowledge of reaction mechanisms and the energy considerations involved.

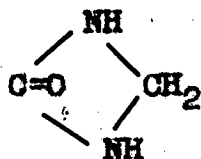
The reaction between urea and formaldehyde first occupied the attention of chemists some sixty years ago with the studies of Hölzer, Lidy, Hemmelmayr, Goldschmidt, Einhorn, Hamburger and others. The greater portion of the work published since then related to the preparative aspects of the reaction and it was not until 1928 that the first serious attempt to suggest a reaction mechanism was made.

Hölzer<sup>2</sup> isolated a compound having the empirical formula  $C_2 H_4 O N_2$  and assigned it the structure:



1. Lapworth, A. J.C.S., 30, 85 (1904).
2. Hölzer, A. Ber., 17, 659 (1884).

Monomethyleneurea is a dehydration product of monomethylolurea  $\text{NH}_2\text{CO.NH.CH}_2\text{OH}$  and Lüdy<sup>3</sup> suggested that its insolubility might be due to the occurrence of a cyclic structure:



Hemmelmayr<sup>4</sup> later prepared a compound which was the same as that obtained by Hölzer and later by Lüdy, by reacting together urea and chloromethyl alcohol.

Important progress in the study of the reaction was made at the turn of the century. However, before reviewing this work it is important to record the factors which influence the urea-formaldehyde reaction. These are:

- (i) the urea to formaldehyde molecular ratio;
- (ii) the solution concentration;
- (iii) temperature;
- (iv) the solution pH;
- (v) catalysts, if present.

These criteria are critical and are responsible for the diversity of products obtained by various workers.

3. Lüdy, L. J.C.S., 56, 1059 (1889).

4. Hemmelmayr, F. von; Monatsch, 12, 89 (1891).



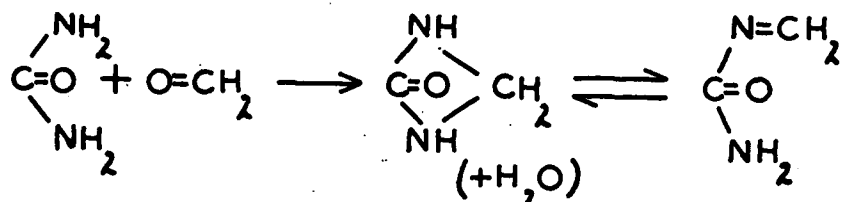
Under mild conditions - low temperatures (e.g. 5-30°C) and neutral or slightly alkaline conditions - important compounds isolated were the crystalline mono- and dimethylolureas.<sup>5,6,7</sup> Einhorn and Hamburger<sup>6</sup> prepared monomethylolurea  $\text{NH}_2\text{CONHCH}_2\text{OH}$ , by reacting urea and formaldehyde in equimolecular proportions in the presence of a small quantity of barium hydroxide at 5°C. Dimethylolurea  $\text{CH}_2\text{OHNHCONHCH}_2\text{OH}$ , was prepared by the same workers using two molecular proportions of formaldehyde to one of urea in the presence of a small quantity of barium hydroxide at 25 - 30°C. The later stages of the condensation were not investigated by these workers, although it was shown that in acid or alkaline solution the methylolureas yielded ill-defined amorphous compounds of varying composition.

Dixon<sup>8</sup> varied the proportions of urea and formaldehyde and effected the condensation in acid solution. Using a urea-formaldehyde molecular ratio of 1:0.75 he obtained a product which, as a result of nitrogen analysis, was believed to be pure methyleneurea.

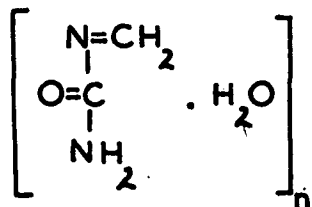
van Laer<sup>9</sup> suggested that at ordinary temperatures the formation of methyleneurea proceeds by the condensation of both the urea amino groups giving a cyclic form

5. Goldschmidt, C. Chem. Ztg., 46, 460 (1897); J.C.S., 74, 178 (1898).
6. Einhorn, A. and Hamburger, A. Ber. 41, 24 (1908).
7. Einhorn, A. Ann., 343, 207 (1905); 361, 113 (1908).
8. Dixon, A.E. J.C.S., 113, 238 (1918).
9. van Laer, M. Bull. Soc. Chim. Belg., 28, 381 (1919).

which then tautomerizes to the asymmetric form:

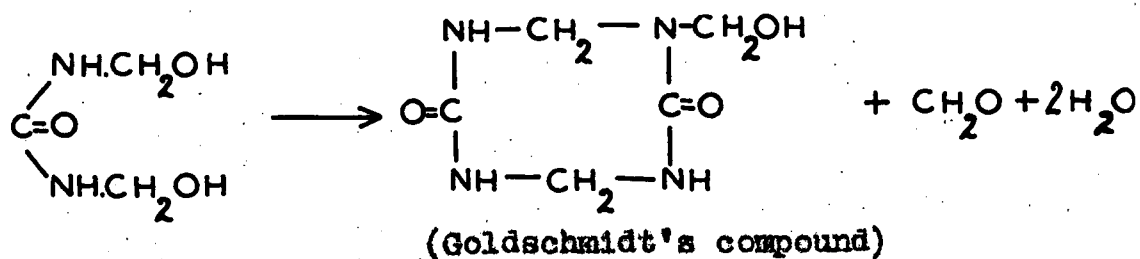


Scheibler and co-workers<sup>10</sup> were of the opinion that a trace of HCl converted the methylolurea first formed into a polymer consisting of methyleneurea units, each containing one firmly bound molecule of water.

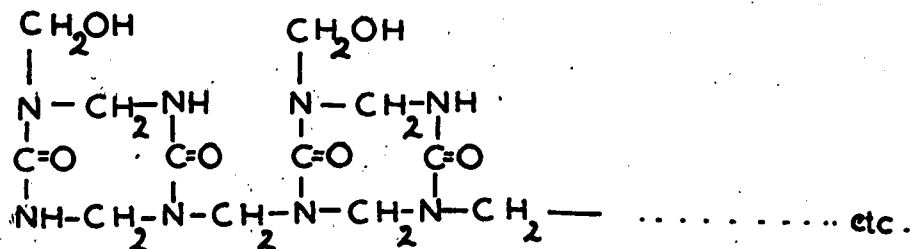


Degradation of the polymers by the same workers led them to believe that they consisted of chains of dimethyleneurea or methylolmethylene units joined together, the free ends of the chains being attached to water molecules. Such chains, they suggested, might be associated by secondary valencies into micelles and colloid particles which confer on the polymerized material its characteristic high molecular physical properties. Scheibler and co-workers also observed that when symmetrical dimethylurea  $\text{CO}(\text{NH} \cdot \text{CH}_3)_2$ , was reacted with formaldehyde, methylol derivatives were formed but no further condensation to methylene compounds took place. It was concluded that the mechanism for the formation of methyleneurea suggested by van Laer was impossible.

Walter and Gewing<sup>11</sup> made an analytical study of the water and formaldehyde lost during the condensation process and early recognised the need for quantitative data. According to Dixon<sup>8</sup>, dimethylolurea loses water and formaldehyde when heated above its melting point to yield a compound which appears to be identical with Goldschmidt's compound<sup>12</sup>;



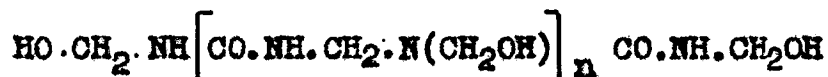
If the formaldehyde split out were taken up again in the formation of a ramified chain the net change of formaldehyde would be zero. Walter and Gewing found that this agreed fairly well with the experimental values; which suggested a chain of the type:



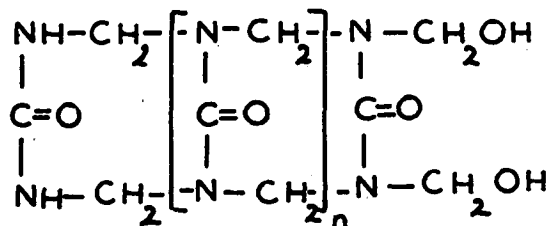
Moreover, as a result of their computations, they decided that the following structures could not be present in the final hardened resin:

11. Walter, G. and Gewing, M. Kolloid - Beihefte, 34, 163 (1936).
12. Goldschmidt, C. Ber., 29, 2438 (1896).

(i) open chain structures of the type:-



(ii) open ring chain structures of the type:-



Very close chemical control would be needed to obtain a homogeneous polymer under the conditions employed by Walter and Gewing. Their findings are inconclusive since with the relatively drastic conditions employed and lack of close control, it is likely that their analytical data represent mean values for mixed structures or structural units.

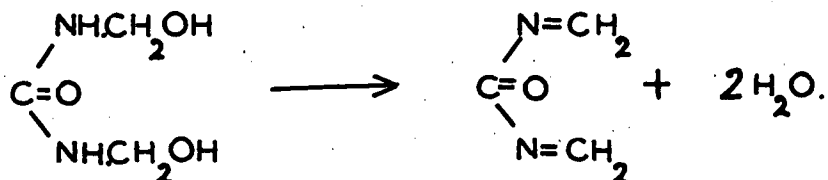
de Chesne<sup>13</sup> examined the urea-formaldehyde condensation by both chemical and physical methods. He suggested that the resins formed when the pH of the reaction mixture is greater than 7, involve the initial condensation of methylolureas and consist of micellar aggregates of linear thread-like molecules of varying degrees of polymerization. It was suggested also that highly solvated hydrophillic colloids are formed which possess the property of irreversible gelation. de Chesne's findings must also receive little support since the reaction was not strictly controlled.

Redfarn<sup>14</sup> commented on the need for strict control of the reaction and suggested that the reason earlier

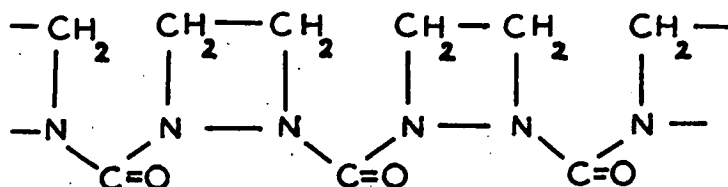
13. de Chesne, E.B. Kolloid-Beihefte, 36, 387 (1932).

14. Redfarn, G.A. British Plastics, 5, 238 (1933).

investigators were at variance, was because of the lack of careful buffering of reaction solutions. He suggested that in acid solution two molecules of water are eliminated from dimethylolurea to yield dimethyleneurea:



heating then results in the formation of a polymer with a saturated chain structure:

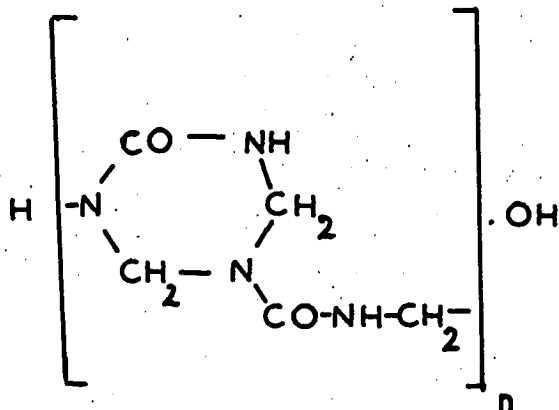
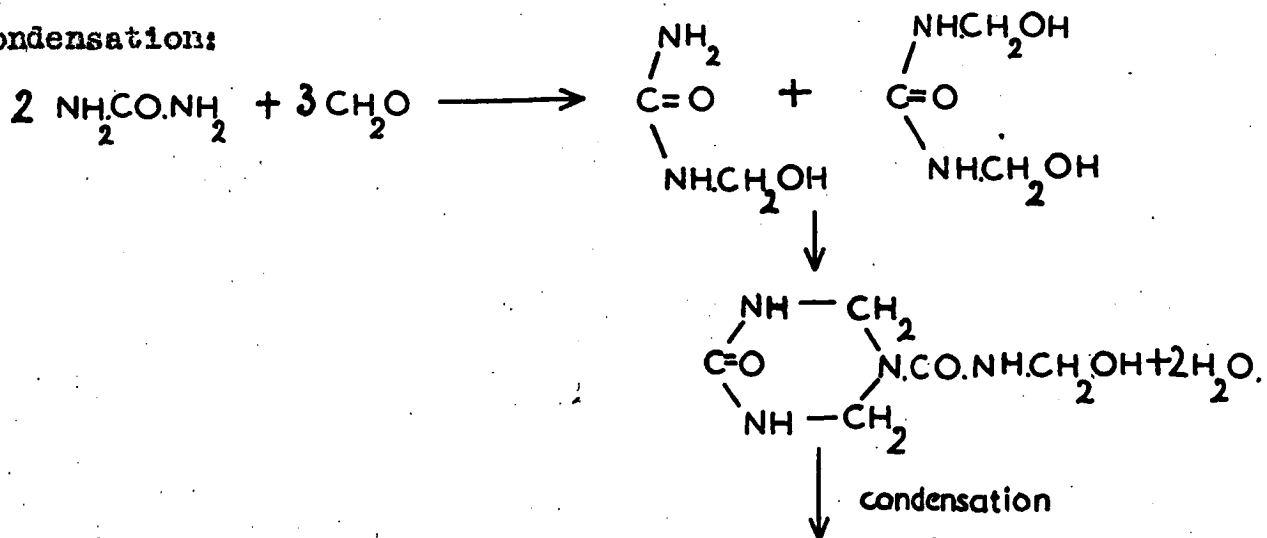


This theory is unsatisfactory since there is no provision for cross-linking and for formaldehyde liberated during the later condensation. Moreover, owing to the strain imposed, the formation of a large number of four-membered rings is unlikely. There is also no mention of the isolation of pure dimethyleneurea itself.

Ellis<sup>15</sup> suggested that two molecules of urea and three of formaldehyde lead to the initial formation of

15. Ellis, C. The Chemistry of Synthetic Resins. Reinhold, New York 1935; U.S.P. 2,115,550.

methylol carbamyl 4-keto hexahydrotriazine, followed by condensation:

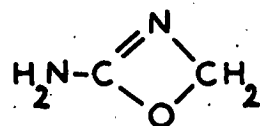


Assuming the above to be correct, gelation can only occur when the ratio of formaldehyde to urea is greater than  $1\frac{1}{2}:1$ , since with smaller quantities insufficient formaldehyde is present to permit necessary cross-linking between secondary amino nitrogens.

Walter<sup>16</sup> studied the condensation further and reported that at high hydrogen ion concentration (pH = 1.0) there occurred rapid deposition of a highly insoluble monomeric

16. Walter, G. Trans. Faraday Soc., 32, 377 (1936).

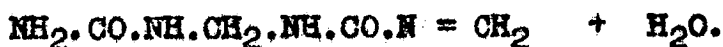
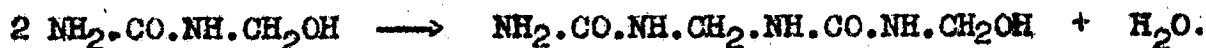
methyleneurea. This compound did not polymerize and he suggested that it had a stable ring structure:



Under less acid conditions (pH = 3.0) the reaction proceeded more slowly giving a methyleneurea which showed a greater tendency to polymerize, and a dimeric and trimeric form. These were suggested to have the following structures:



The formation of these polymeric substances were supposed to take place through the initial formation of methylol compounds as follows:



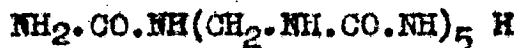
The evidence is somewhat inconclusive, since molecular weights of products were determined by the cryoscopic method using formic acid as the solvent. Short chain methylol and methylene compounds are very sensitive to formic acid being rapidly converted to polymeric compounds even at low temperatures. In addition, since the number of free  $\text{-NH}_2$  groups was determined by reacting the products with nitrous acid, it is likely that the nitrous acid would promote further polymerization and cross-linking giving false values.

A similar effect has been observed with condensation products of urea and formaldehyde and the hydrochloric acid set free from hydroxylamine hydrochloride which was used as an analytical reagent.<sup>17</sup>

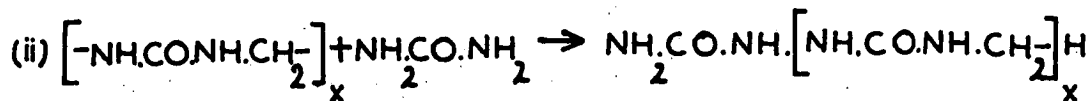
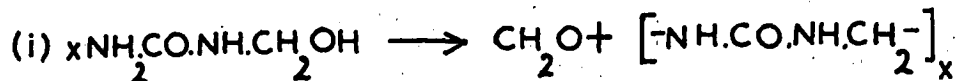
Kadowaki<sup>18</sup> reacted urea and formaldehyde in the molecular ratio 8:1 in the presence of hydrochloric acid and obtained methylenebisurea, m.p. 218°C, which was also obtained by Vass:<sup>19</sup>



Kadowaki found that aqueous solutions of methyleneurea when acidified gave insoluble polymethyleneureas such as pentamethylenehexaurea:



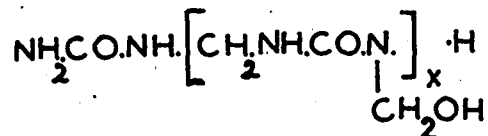
On the basis of these reactions Kadowaki suggested that with one molecule of urea and one or less of formaldehyde, a chain condensation occurs;



17. Smythe, L.E. J. Phys. Colloid Chem., 51, 369 (1947).
18. Kadowaki, H. Bull. Chem. Soc. Japan, 11, 248 (1936).
19. Vass, F. British Plastics, 10, 115 (1938).



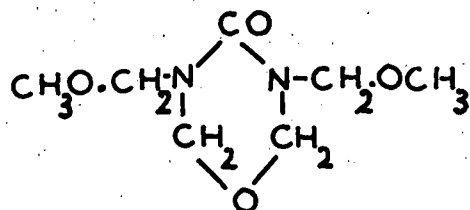
With one molecule of urea and more than one molecule of formaldehyde the condensation proceeds in a similar manner giving linear chains with attached lateral methylol groups:



The methylol groups would then be in a position to react with adjacent secondary amino groups in other chains to give methylene cross linkages.

Kadowaki also succeeded in isolating both mono- and dimethylol derivatives of methylenebisurea and these could be converted by heating to a hard transparent resin.

With one molecule of urea to four of formaldehyde at ordinary temperatures in the presence of  $\text{Ba}(\text{OH})_2$  and subsequent addition of methanol and excess of  $\text{HCl}$ , Kadowaki isolated 3:5 dimethoxymethyluron:



This compound may be regarded as being derived from a tetramethylurea in which two methylol groups have been methylated and the other two have undergone intra-molecular condensation with the formation of an ether group. Kadowaki's findings are interesting and give a partial picture of the reaction under some conditions. It is disappointing however, to find that lack of careful control of the reaction

particularly when strong condensing agents are employed<sup>20</sup> leads to the formation of ill-defined compounds.

Hodgins and Hovey<sup>21</sup> applied Kienle's theory of functionality<sup>22</sup> to the formation of urea-formaldehyde condensation products. In the case of monomethylolurea it was suggested that only long-chain or branched polymers are permissible and no cross-linkage takes place. For dimethylolurea there is an equal number of hydrogen and hydroxyl reactive points and three-dimensional polymers with cross-linkages can be formed. Experiments suggested that in the case of mixtures of monomethylol and dimethylol ureas, the cross linking tendency increased with increasing proportion of dimethylolurea. In this case the effective functionalities of the two methylolureas depend on the relative proportions of each component present. This view of the condensation is valuable when considering the initial condensation and fate of the methylolureas, once formed.

Vogel<sup>23</sup> carried out viscosity and osmotic pressure measurements which suggested that for condensations of urea and formaldehyde in 1:1 molecular ratio the macromolecules are approximately spherical in shape with three dimensional branched chain formations present.

20. Smythe, L.E. J.A.C.S. IV Reactions of Methylenebisureas.

75, 1953 (in press)

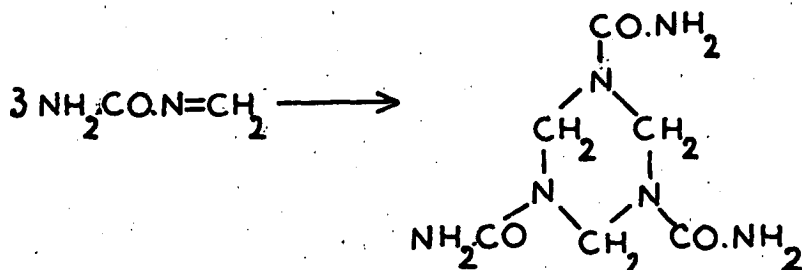
21. Hodgins, T.S. and Hovey, A.G. Ind. Eng. Chem., 31, 673 (1939).

22. Kienle, R.H. Ind. Eng. Chem., 22, 590 (1930).

23. Vogel, R.E. Kunststoffe, 31, 309 (1941).

Marvel<sup>24</sup> and co-workers regard urea as containing an amino and an amido group and suggest that resinification proceeds as follows:

- (i) the initial reaction is between the primary amine part of the molecule and the formaldehyde to give a methylene-imine derivative which immediately trimerizes;



- (ii) the amide groups then react with more formaldehyde to form methylene cross linkages between the rings.

Marvel supports his theory with rather inconclusive evidence since the trimer postulated has never been isolated. In addition it must be emphasised that figures for the nitrogen content of the resins ranging from 33 - 36% mean little unless the conditions of condensation be subject to very close control. It is possible that the highly condensed systems investigated by various workers contain shorter open chain structures together with the more abundant branched and cross-linked structures already discussed. Hydration of formaldehyde, urea and the lower molecular weight methylol and methylene compounds should not be overlooked and this

24. Marvel, C.S., Elliott, J.R., Boettner, F.E. and Yaska, J. J.A.C.S., 68, 9 (1946).

may well lead to the variation in analytical determinations of water and formaldehyde by Walter.<sup>16</sup>

At this stage it is not proposed to consider further the few theories advanced during the past four years and relating to the resinification process, since it is the kinetic and quantitative aspects of the initial condensation which concerns this investigation. What has been said will be sufficient to serve both as an introduction to the kinetic studies and provide a broad view of the field into which these studies fit. In addition, no significant advance has been made during the past four years and recent studies significantly concern the kinetics of the initial condensation. Because of the number of factors mentioned earlier which influence the reaction, progress must necessarily be slow until the overall picture is completed. With careful control of the reaction and statement of conditions, there is room for further serious investigation and the recording of quantitative data.

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KINETICS OF THE FORMATION OF SUBSTITUTED DIAMIDES  
OF CARBONIC ACID

Presented as

Urea-Formaldehyde Kinetic Studies

Part I. Variation in Urea Solutions.

Part II. Factors Influencing Initial Reaction.

Part III. Polarographic Studies in Dilute Solution.

Part IV. Reactions of Methylenebisureas.

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Smythe, L.E., 1951, Urea—formaldehyde kinetic studies. I. Variations in urea solutions, *Journal of the American Chemical Society*, 73(6), 2735-2738  
[10.1021/ja01150a089](https://doi.org/10.1021/ja01150a089)

Smythe, L.E., 1952, Urea—formaldehyde kinetic studies. II. Factors influencing initial reaction, *Journal of the American Chemical Society*, 74(11), 2713-2715 [10.1021/ja01131a006](https://doi.org/10.1021/ja01131a006)

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRYUNIVERSITY OF TASMANIA.UREA FORMALDEHYDE KINETIC STUDIES.III. POLAROGRAPHIC STUDIES IN DILUTE SOLUTION.

By Lloyd E. SMYTHE.

**Abstract:**

The reaction between (a) urea, (b) N-methylurea, (c) N-ethylurea and formaldehyde has been studied in dilute solution at pH 7.15 using the polarographic method for following the concentration of unreacted formaldehyde. The reactions were found to be second order and rate constants and energies of activation have been evaluated. Differences have been observed in the reaction of urea with formaldehyde as compared with the simple N-alkyl ureas and formaldehyde. It is suggested that in the case of alkyl ureas some effective resonance stabilization is lost and the effect becomes more pronounced in dilute solution resulting in increased reactivity. Hydration of both the urea and formaldehyde is appreciable in the region of pH 7; the reactions reaching a certain stage and being unable to proceed further. The effect of acid or alkaline condensing agents in dilute solution would be initially to break down forces of hydration and in the case of alkaline solutions the reaction is reversible. The initial rapid reaction previously observed becomes less important with increasing dilution and the significance of this is discussed. The polarographic method for estimating formaldehyde is given in some detail since it has been found suitable for following the course of industrially used condensations.

Part II of this series<sup>1</sup> indicated that dilution of reactants exerted a considerable influence on the nature of the initial reaction between urea and formaldehyde. It was also evident that the analytical method for the estimation of formaldehyde<sup>2</sup> was subject to some errors when working with dilute solutions.

A study of the reaction in dilute solution using urea and N-alkyl ureas was commenced. The polarographic method appeared to be the most suitable in this case and Crowe and Lynch<sup>3</sup> had successfully used it employing 0.05N lithium hydroxide and buffers giving supporting electrolyte pH values from 8.6 - 12.7. In all cases the reaction was shown to be reversible and equilibrium constants were evaluated. Earlier observations<sup>4</sup> had indicated that while most alkaline condensing agents are effective for the formation of methylol compounds there was evidence of some hydrolysis of the condensation product, equilibrium evidently being attained, particularly at pH values greater than 9.0. In this study it was desirable that the pH of the supporting electrolyte be maintained as close as possible to 7, so as not to influence materially the forward or reverse reactions. The effect of phosphate buffers on the reaction has been studied<sup>1</sup> and preliminary studies using different supporting electrolytes indicated that Sørensen buffer of seven parts by volume of  $\frac{M}{15} Na_2 HPO_4$  and three parts by volume of  $\frac{M}{15} KH_2 PO_4$  giving a pH of 7.15 at 25°C, provided a suitable supporting electrolyte.

1. Smythe, L.E. This Journal, 74, 2713 (1952).
2. Smythe, L.E. J. Phys. and Colloid Chem., 51, 396 (1947).
3. Crowe, G.A. and Lynch, C.C. This Journal. 70, 3795 (1948);  
71, 3731 (1949);  
72, 3622 (1950).
4. Smythe, L.E. Unpublished work.



It is well known<sup>5</sup> that polarographic limiting currents on buffered solutions of formaldehyde show an exceptional dependence on pH. At neutrality the limiting current is less than  $\frac{1}{100}$  and at pH 13.5 less than  $\frac{1}{5}$  of the diffusion current as calculated by the Ilkovic equation. Nevertheless the diffusion current in the selected buffer, although reduced, was adequate giving smooth polarographic steps with mostly no maxima and thus avoiding the use of maximum suppressors.

#### EXPERIMENTAL.

The polarographic measurements were made with a Tinsley ink recording polarograph (V722/1) employing D.C. amplification of the current passing through the solution in the polarographic cell. The recorder unit was a moving coil D.C. pen type milliammeter, the standard speed being 1 inch per minute corresponding to a voltage change of 0.5 volts. The "capillary constant"  $K$  was 23.82 using 0.1 M  $\text{CH}_2\text{O}$  in Sørensen buffer containing dissolved air; applied voltage -1.65 v., head of mercury 501 m.m., drop time 2.52 sec., temperature 25°C. The radius of the capillary orifice<sup>6</sup>  $\rho$  determined in 0.1 M KCl at 25°C using an open circuit was 25 microns.

With Sørensen buffer supporting electrolyte containing dissolved air, the half-wave potential vs. the mercury pool electrode was -1.65 volts and -1.73 volts vs. the saturated calomel electrode. Concentration of formaldehyde within the range 0.01 - 0.10 M exhibited this half wave potential but concentrations of 0.10 - 0.50 M resulted in a shift to a

5. Veseley, K. and Brdicka, R., Czech.Chem.Communs. 12, 313 (1947).
6. Müller, O.H. The Polarographic Method of Analysis, pp.182-190, Chem.Educ.Pub.Co. (1951).

slightly more negative potential. Figure 1 shows the relation between the diffusion current in microamperes and concentration expressed as molarity.

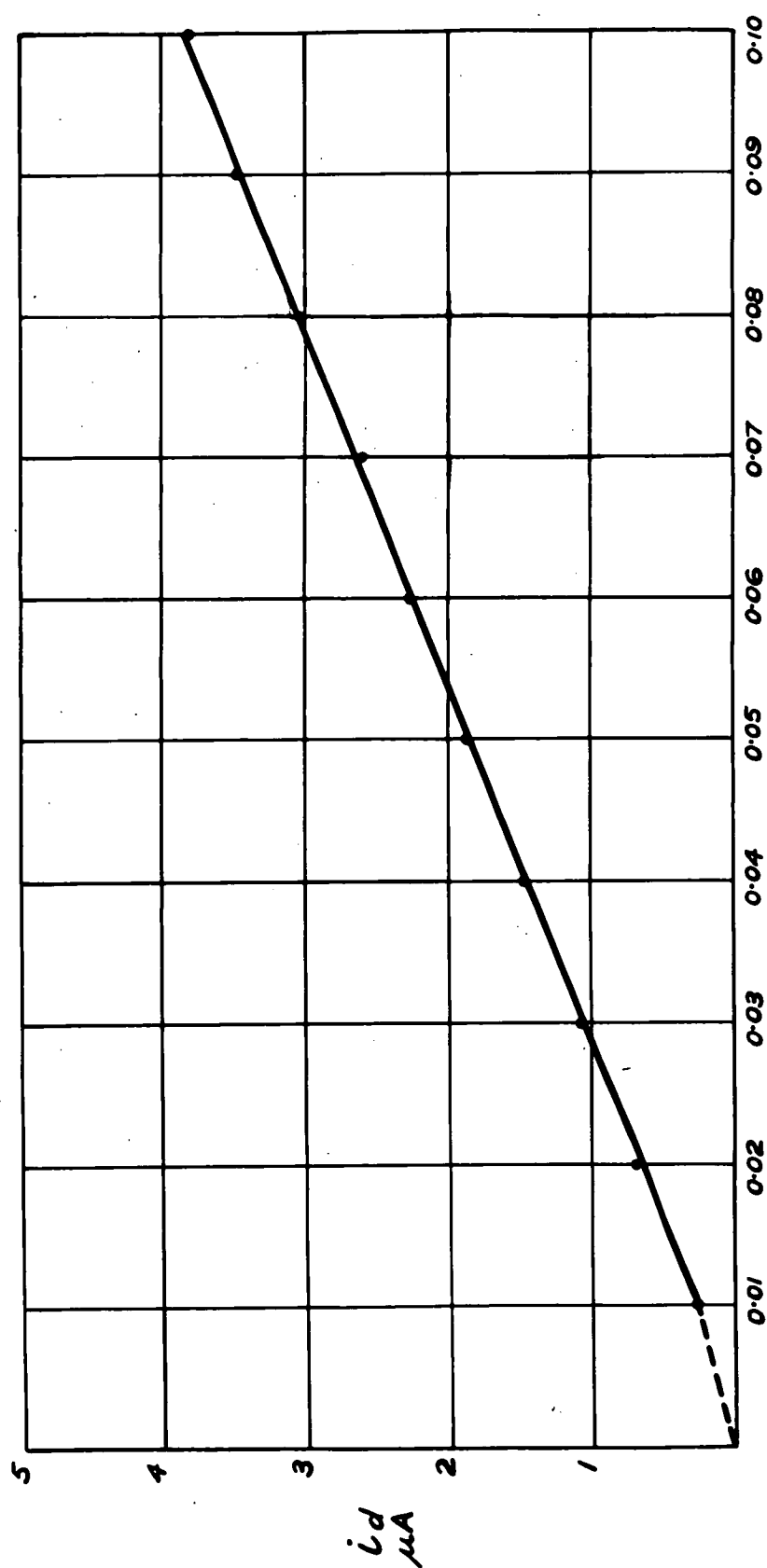
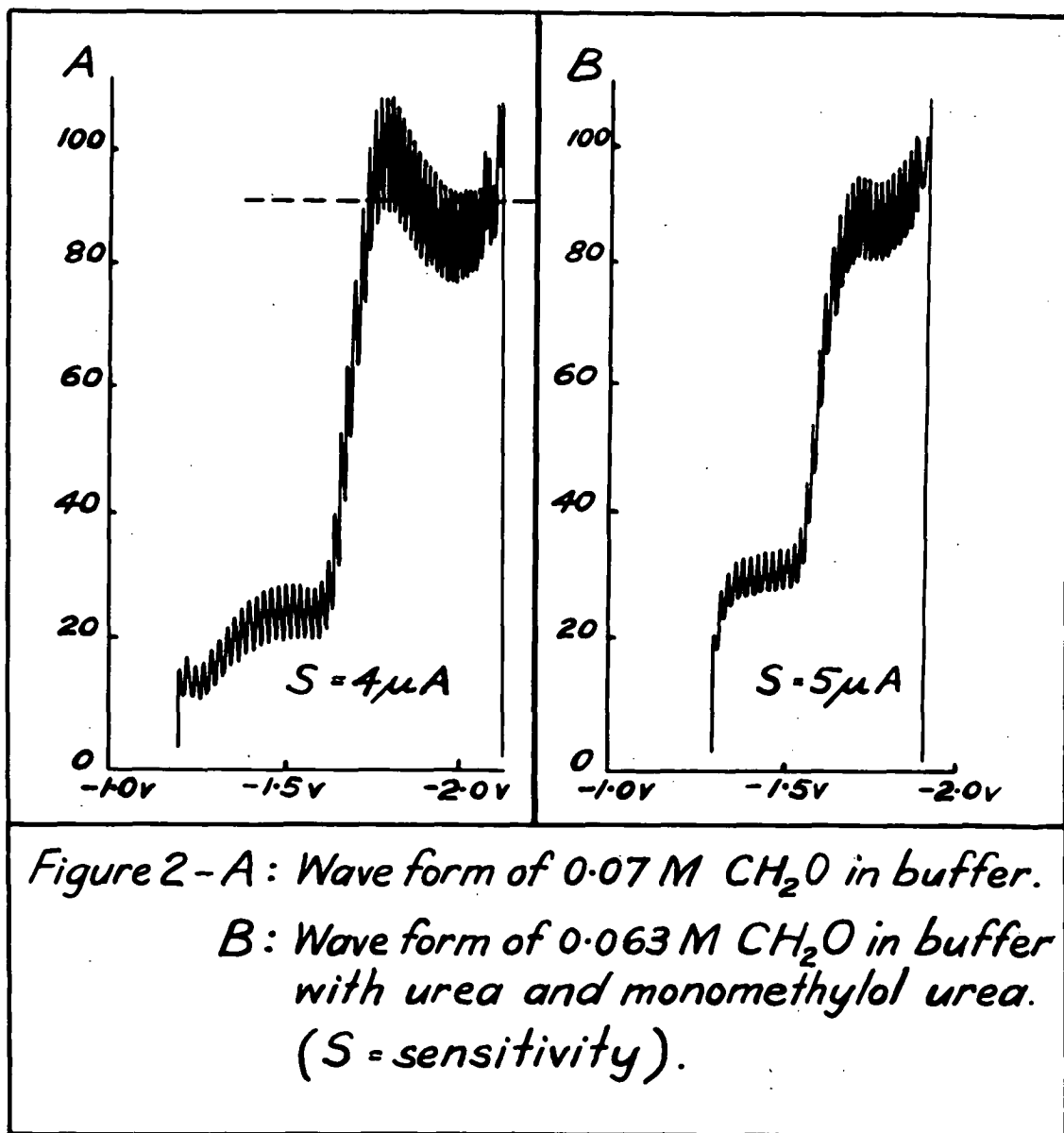
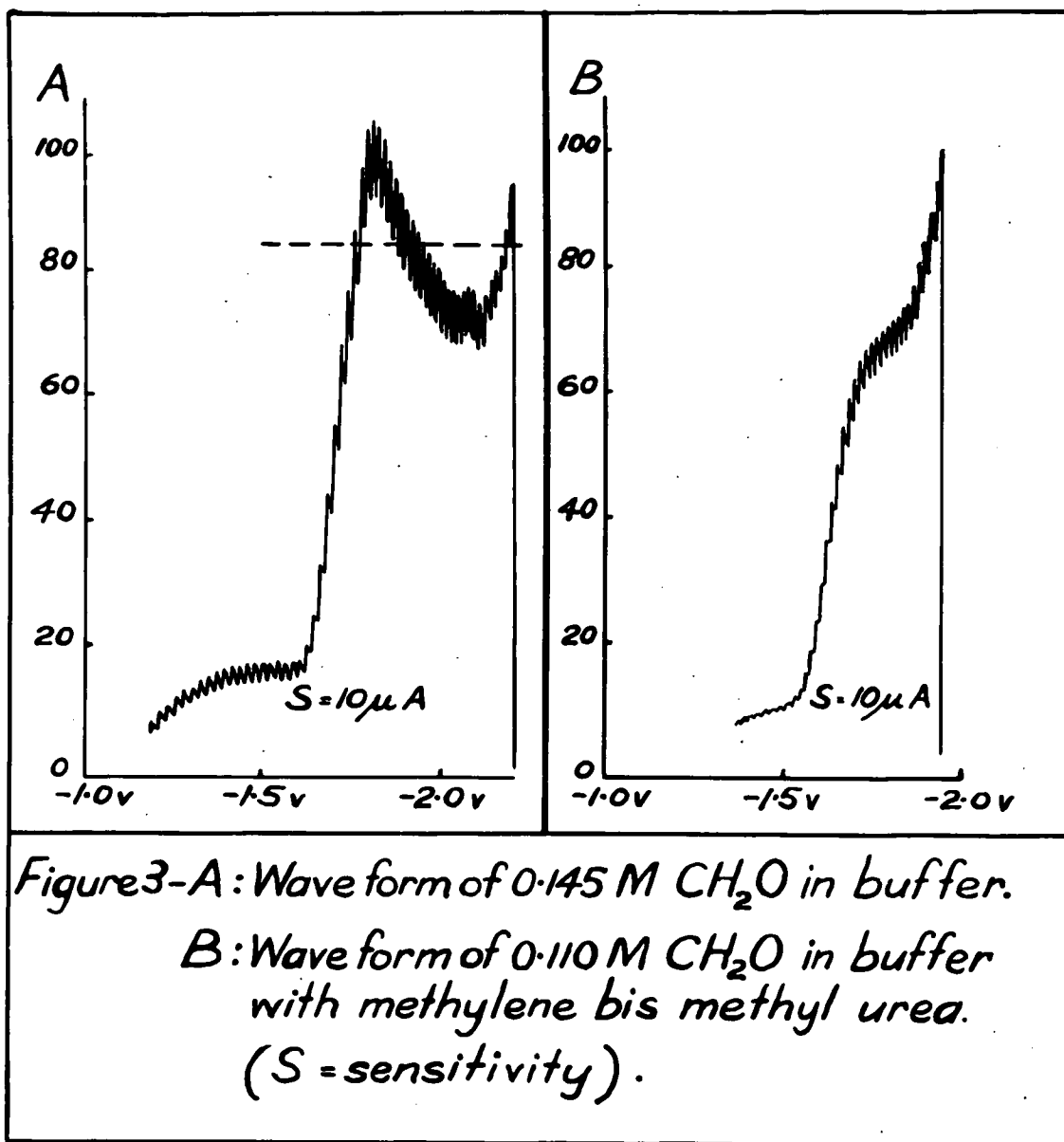


Figure 1 - Molar concentration formaldehyde vs. diffusion current (microamperes).

Sensitivities corresponding to full scale deflection on the recording chart were selected to give the largest possible step. Accuracy of measurement was  $\pm 0.05\mu\text{A}$  over the range 0.01 - 0.10 M  $\text{CH}_2\text{O}$ . Slight maxima were exhibited with formaldehyde alone in the buffer and it was not found necessary to eliminate these as step heights were reliably determined by drawing a line representing the limiting current as shown in Polarogram A, Figure 2. In this case other means for estimating the diffusion current did not prove as reliable as the method employed. It is interesting to note that in the studies of the reaction mixture of urea and formaldehyde, the urea in each case acted as a maximum suppressor giving a well defined step shown in Polarogram B, Figure 2.





Some studies carried out with 0.10 - 0.50 M formaldehyde solutions revealed that the maxima exhibited offered some difficulty in measurement of diffusion current (Polarogram A, Figure 3). Although these maxima were also effectively suppressed in the presence of urea and substituted ureas, (Polarogram B, Figure 3) the accuracy was only of the order  $\pm 0.2\mu\text{A}$ . The maxima in all cases appeared to be  $2.5\mu\text{A}$  greater than the line drawn through the step and used for measuring the diffusion current.

As dissolved oxygen was not removed from any of the solutions, zero suppression was used in the range 0.01 - 0.10 M  $\text{CH}_2\text{O}$ , the recorder zero adjustment being used to depress the oxygen step. Zero suppression was not found necessary in the range 0.10 - 0.50 M  $\text{CH}_2\text{O}$ , using lower sensitivities. The polarograph cell used was a modification of the simple Heyrovsky cell, holding 4 ml. of solution. Temperature control was by means of a thermostat bath to within  $\pm 0.05^\circ\text{C}$ . The height of mercury above the capillary orifice was maintained constant by a levelling device.

The polarographic procedure outlined above has been used to follow the progress of urea - formaldehyde condensations on the industrial scale. The dilution of the sample taken with buffer, effectively retards the reaction rate and prevents elimination of formaldehyde already combined, as may be the case with other supporting electrolytes. The progress of a typical condensation employing 500 parts by weight 40 per cent  $\frac{\text{W}}{\text{V}}$  formalin, 185 parts by weight urea, one part by weight  $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$  was followed by withdrawing 1 ml. samples and adding to 110 ml. buffer solution at  $25^\circ\text{C}$ . The polarogram was taken

using 4ml. of this solution, the concentration of free formaldehyde being estimated from Figure 1.

Chemicals used were of analytical reagent grade or specially purified in the case of urea<sup>7</sup>. N-methyl and N-ethyl ureas were prepared by the method of Davis and Blanchard<sup>8</sup>.

Table I.

DATA FOR THE REACTION BETWEEN EQUIMOLAR (0.1M) AMOUNTS OF FORMALDEHYDE AND UREAS.

Temp °C	No. of experi- ments	Urea	k 10 <sup>4</sup> l.mole <sup>-1</sup> sec <sup>-1</sup>	a	CH <sub>2</sub> O used 1st. 300 sec. %.	End of Reaction M conc. CH <sub>2</sub> O	ΔEa (approx.)
0.05							
25	7	NH <sub>2</sub> CONH <sub>2</sub>	1.7 (14,000)		1.0	0.035	15,300
35	5	NH <sub>2</sub> CONH <sub>2</sub>	3.8 (12,000)		1.0	0.032	
25	8	MeNHCONH <sub>2</sub>	8.3 (8,000)		7.5	0.050	14,100
35	6	MeNHCONH <sub>2</sub>	18.0 (6,000)		8.0	0.047	
25	6	EtNHCONH <sub>2</sub>	7.0 (10,000)		7.0	0.054	14,000
35	4	EtNHCONH <sub>2</sub>	15.5 (9,600)		7.4	0.051	

a k equals average for number of seconds in parenthesis minus 300.

b In calories. Evaluated for two temperatures only owing to loss of CH<sub>2</sub>O at temperatures greater than 35°C.

7. Smythe, L.E. This Journal, 73, 2735 (1951).

8. Davis, T.L. and Blanchard, K.C., *ibid*, 51, 1790 (1929).



The reactions were second order. Important effects were:-

Effect of Dilution - For urea and formaldehyde in equimolar proportions at 25°C, previous results<sup>1,2,7</sup> together with those given in Table I show that for pH values close to 7, rate constants increase with increasing dilution of reactants attaining maximum values with 0.5 M solutions and falling off as dilution increases further. Anion formation of urea may increase with dilution attaining limiting values in the region of 0.5 M solutions. Thereafter competition for the nucleophilic nitrogen of urea involves increasingly stronger forces of hydration of the urea molecule. Formaldehyde would be fully hydrated<sup>2</sup> under these conditions of pH and dilution and depolymerization would not be involved. For 0.1 M solutions the percentage of formaldehyde reacted in the first 300 seconds now reduces to less than 1 per cent as compared with much higher percentages for stronger solutions<sup>2</sup>. The reaction is now of the slow bimolecular variety from zero time. Crowe and Lynch<sup>3</sup> have shown that increasing hydroxyl ion concentration results in higher rate constants. This would increase dehydration of both the methylene glycol and urea thus resulting in relatively higher rates as compared with those in Table I. In the same table it is shown that the reaction does not go to completion under the conditions stated. At pH 7 the reaction is not reversible but is second order from zero time until 65 per cent of the formaldehyde has been used up, thereafter no reaction takes place since forces of hydration cannot be overcome. This has been confirmed by allowing the reaction mixture to stand for several days after the 65 per cent stage had been attained;

no further reaction took place. In addition monomethylolurea, methylenebisurea, methylenebismethylurea and monomethylolmethylenbisethylurea showed no signs of hydrolysis<sup>9</sup> in the buffer over periods of up to three weeks at 25°C. At pH greater than 8.6 Crowe and Lynch<sup>3</sup> have shown the reaction to be reversible and thus while increased hydroxyl ion concentration increases the reaction rate in dilute solution it also promotes hydrolysis of the reaction product possibly preceded by dehydration.

For N-methylurea the rate constant relationship between urea and N-methylurea which was approximately 6 to 1 in the case of 8 M solutions becomes reversed and the reaction with N-methylurea is now five times more rapid. This feature of the reaction which also holds for N-ethylurea is discussed under the heading reaction mechanism.

Column 5, Table I shows that a higher percentage of formaldehyde is utilised in the first 300 seconds in the case of both N-methylurea and N-ethylurea, as compared with urea. This fits in with the fact that the alkyl ureas lose resonance stabilization as compared with urea and the rate of anion formation is increased. The effect becomes more pronounced with increasing dilution since both urea and the alkyl ureas are very weak bases. The relative effect in the case of the alkyl ureas is greater even though anion formation may reach limiting values in the region of 0.5 M solutions. In the case of the alkyl ureas examined, only approximately 50 per cent of the formaldehyde combines and it is thought that two effects are important in this case. Methylenebisureas may be the principal reaction

products, involving the utilization of all the urea and half of the formaldehyde. When formed, no further reaction of the methylenebisureas with the formaldehyde takes place owing to both hydration and the greater difficulty of the reaction between formaldehyde and the nitrogen with the attached alkyl group. The reaction is not reversible and will not proceed further even after periods of days.

It will be appreciated that the above considerations apply to mono- and disubstituted ureas and the fact that dimethylureas will not give dimethylol derivatives and triethylurea will not react with formaldehyde at all<sup>10</sup> is additional evidence that structure of urea plays an important part in determining the reactivity of these derivatives.

For N-ethylurea the rate constant for 8 M solutions and not recorded in Part II, was found to be  $1.6 \times 10^{-5} \text{ l.mole}^{-1} \text{ sec}^{-1}$ . (30°C) with 42 per cent of the formaldehyde utilised in the first 300 seconds and  $\Delta E_a$  15,900 calories. This may be compared with data for urea and N-methylurea given in Table I and previously.<sup>1,2,7.</sup>

Effect of Buffer.- It has been shown previously that the addition of an acid phosphate buffer increases the reaction rate. However, since the relative increase is known and results are compared using the one medium in the case of dilute solutions, the presence of the buffer should not materially affect the conclusions to be drawn.

Energy of Activation. -  $\Delta E_a$  appears to be of the same order as previous determinations.<sup>1,2,3,7.</sup> Even though the

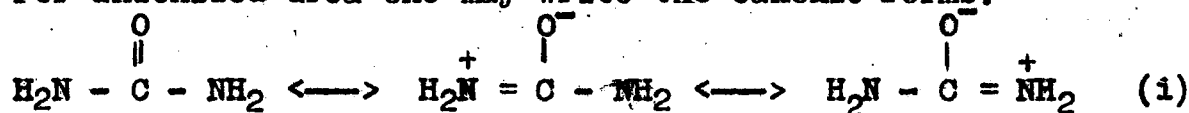
10. Einhorn, A., Ann., 361, 113-165. (1908).

energies of activation are only accurate to approx.  $\pm 1000$  calories per mole it is interesting to note that the values are somewhat lower for the alkyl ureas.

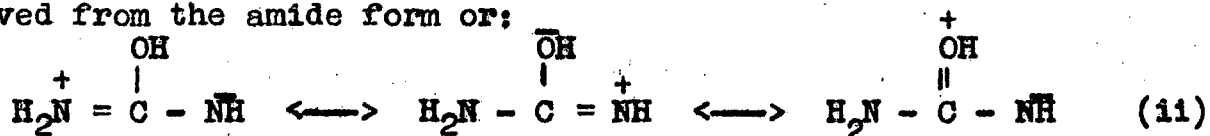
### Reaction Mechanism and Substitution in the Urea Molecule.

The nucleophilic nitrogen of urea must attack the electrophilic carbon centre of formaldehyde to afford N-methylolureas, methylenebisureas etc.<sup>1,2,3,7</sup>. Tautomeric and/or mesomeric forms enhancing the nucleophilic nature of the reactive nitrogen are more likely to be involved in the reaction than others. A similar attack by nucleophilic oxygen is less important since this would lead to the formation of unstable compounds and an equilibrium strongly displaced in favour of the original reactants.

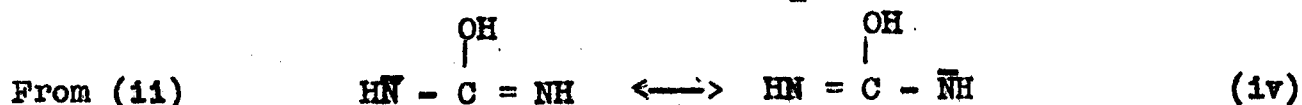
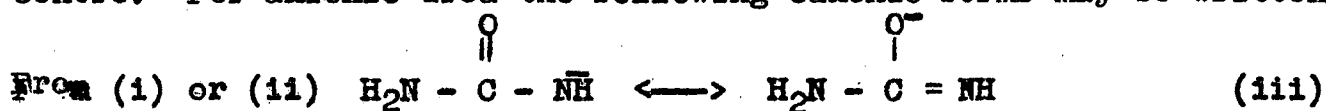
For unionized urea one may write the canonic forms:



derived from the amide form or:

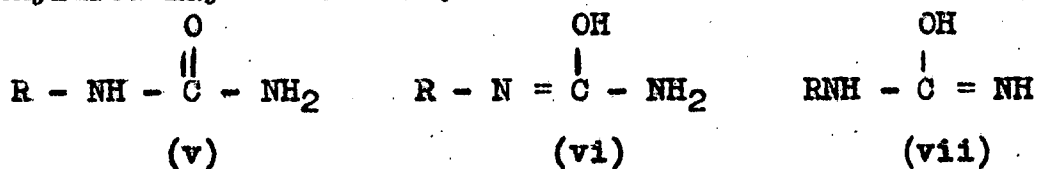


from the imidol form. The amide structure is seen to be more important partly owing to the possibility of equivalent canonic forms, partly owing to a more probable type of charge distribution. In this form however, the nitrogen is deactivated as a nucleophilic centre. For anionic urea the following canonic forms may be written

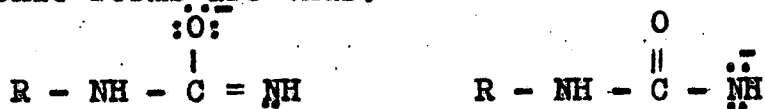


(iv) has more resonance stabilization than (iii) owing to equivalent canonic forms; it also appears to have nitrogen activated for nucleophilic reactions. On these considerations (i) is predominating over (ii) under static, i.e. non-reacting conditions. The anionic forms necessary for the initial condensation are evidently obtained mainly through the ionization of (ii). In other words, (ii) is a stronger acid than (i), since the former gains resonance energy on ionization to the anionic forms (iii) and (iv), mainly to (iv). Under acidic conditions therefore, the distinction between (i) and (ii) disappears and the N-methylol type of condensation is no longer favoured.

The tautomeric forms of a simple alkyl urea such as N-methylurea may be written:



With R = Me or Et, the inductive effect is towards the adjacent nitrogen and (vi) is less likely than (vii). The principal anionic forms are thus:



It is seen that both the unionized and ionized forms of the alkyl ureas lose resonance stabilization in comparison with corresponding forms of urea and this may be responsible for the increased reactivity since there is less resonance energy to lose on combining with formaldehyde. In this case the alkyl ureas would show increased values of k and decreased values

for  $\Delta E_a$  against urea. The results tend to confirm this view.

It would be expected that substitution of Et for Me would increase this effect so that N-ethylurea should show slightly higher values for  $k$  than N-methylurea. Table I however, does not indicate any significant difference between the behaviour of N-methyl and N-ethylurea. An examination of the behaviour of a larger series of alkyl ureas might illustrate this trend more clearly.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY.UNIVERSITY OF TASMANIA.UREA-FORMALDEHYDE KINETIC STUDIES.IV. REACTIONS OF METHYLENEBISUREAS.

By Lloyd E. SMYTHE.

Abstract:

The stability and reactions of methylenebisureas with formaldehyde in dilute neutral and alkaline solutions has been investigated. Hydrolysis of methylenebisureas proceeds in alkaline solution ( $\text{pH} = 12.7$ ) but not in neutral solution ( $\text{pH} = 7.15$ ) where the molecule is hydrated. The effect of alkali is to break down the forces of hydration. It was found that methylol groups are more easily hydrolysed than methylene linkages. In neutral solution methylenebisureas do not react with formaldehyde owing to both hydration of the molecule and lack of strongly nucleophilic nitrogen centres.

In the course of studies of the reaction of dilute solutions of urea and simple N-alkylureas with formaldehyde at  $\text{pH} 7.15$  it was observed that certain methylenebisureas once formed, showed no sign of hydrolysis, further condensation or polymerization.<sup>1</sup> Methylene compounds have been postulated as important units in urea-formaldehyde plastics and it was desirable that the reactions of methylenebisureas be studied further. It was found that the polarographic method of analysis used previously<sup>1</sup> was more suitable for this study than titration methods. The use of titration methods for the

estimation of formaldehyde when working with more concentrated solutions must receive careful consideration, since condensation products have been shown to influence the estimation<sup>2</sup>.

Preliminary studies have indicated that methylol compounds<sup>2</sup>, methylenebisureas and more highly condensed systems each have separately different effects on the usual titration methods. Consequently the study of later stages of condensation in more concentrated solution must await reliable analytical methods. Borzee and Smets<sup>3</sup> have recently used titration methods in a study of condensation reactions of urea and formaldehyde in concentrated solution but do not state whether errors were introduced by the condensation products.

#### EXPERIMENTAL.

The apparatus and general technique used in this study have been described<sup>1</sup>. Compounds prepared were:-

monomethylolurea  $\text{NH}_2\text{CONHCH}_2\text{OH}$ , m.p.  $111^\circ\text{C}$ , Einhorn and Hamburger<sup>4</sup>;  
 methylenebisurea  $\text{NH}_2\text{CONHCH}_2\text{NHCONH}_2$ , m.p.  $218^\circ\text{C}$  decomp., Kadowaki<sup>5</sup>;  
 methylenebismethylurea  $\text{CH}_3\text{NHCONHCH}_2\text{NHCONHCH}_3$ , m.p.  $184^\circ\text{C}$ , Kadowaki<sup>5</sup>;  
 methylenebisethylurea  $\text{C}_2\text{H}_5\text{NHCONHCH}_2\text{NHCONHC}_2\text{H}_5$ , m.p.  $117^\circ\text{C}$ , Einhorn<sup>6</sup>;  
 monomethylolmethylenebisethylurea  $\text{C}_2\text{H}_5\text{NHCON}(\text{CH}_2\text{OH})\text{CH}_2\text{NHCONHC}_2\text{H}_5$ ,  
 m.p.  $171^\circ\text{C}$ , Einhorn<sup>6</sup>. It was found necessary to modify several

2. Smythe, L.E. J. Phys. Colloid Chem., 51, 396 (1947).
3. Borzee, A. and Smets, G. J. Poly. Sci., 8, 371 (1952).
4. Einhorn, A. and Hamburger, A. Ber., 41, 24 (1908).
5. Kadowaki, H. Bull. Chem. Soc. Japan, 11, 248 (1936).
6. Einhorn, A. Ann., 361, 113 (1908).



of the above methods of preparation where hydrochloric acid was used as condensing agent. Where the solutions were allowed to develop excessive heat during the initial reaction, ill-defined products of indefinite melting point were obtained. These would not respond to purification.

The stability of methylenebisureas in dilute solution (Sørensen buffer) was tested as follows: 0.1 M solutions of the compounds listed above were prepared with the buffer. The solutions were allowed to stand in sealed tubes at temperatures of 25°C and 35°C. No free formaldehyde was detected by polarographic analysis at any time up to three weeks.

The reaction of methylenebisureas with formaldehyde was also studied. 0.2 M solutions of the compounds listed above, prepared with Sørensen buffer, were allowed to react with equal volumes of 0.2 M solutions of formaldehyde in the same buffer at temperatures of 25°C and 35°C. For periods of up to three weeks the concentration of free formaldehyde remained unaltered at 0.1 M.

Methylenebisureas were found to be unstable in the presence of a strong base. In this case, lithium hydroxide was selected as the base, since it would provide for comparison of the results with those of Crowe and Lynch<sup>7</sup>. Equal volumes of 0.2 M solutions of the compounds listed above and 0.1 N LiOH were reacted together at 25°C with the results given in Table I. The decompositions were first order from zero time.

7. Crowe, G.A. and Lynch, C.C. This Journal, 70, 3795 (1948).

Table I.

Urea	CH <sub>2</sub> O liberated	% CH <sub>2</sub> O at equilibrium	k x 10 <sup>3</sup> sec. <sup>-1</sup>
NH <sub>2</sub> CONHCH <sub>2</sub> OH	rapid	85 <sup>a</sup>	1.40
NH <sub>2</sub> CONHCH <sub>2</sub> NHCONH <sub>2</sub>	slow	75	0.08
CH <sub>3</sub> NHCONHCH <sub>2</sub> NHCONHCH <sub>3</sub>	slow	70	0.06
C <sub>2</sub> H <sub>5</sub> NHCONHCH <sub>2</sub> NHCONHC <sub>2</sub> H <sub>5</sub>	slow	70	0.07
C <sub>2</sub> H <sub>5</sub> NHCON(CH <sub>2</sub> OH)CH <sub>2</sub> NHCONHC <sub>2</sub> H <sub>5</sub>	rapid	87 <sup>b</sup>	0.60

a. after 60 minutes. b. after 140 minutes refers to 87 per cent of the CH<sub>2</sub>O available from the methylol group; CH<sub>2</sub>O from the methylene group being liberated slowly thereafter.

#### DISCUSSION.

Previous results<sup>1</sup> together with the above lead to the following conclusions. In the reaction of equimolar (0.1 M) solutions of simple N-alkyl ureas with formaldehyde under the conditions stated, methylenebisureas are the principal products of the reaction. The reaction of methylenebisureas with additional formaldehyde is not possible owing to hydration of the urea molecule. These ureas were found to be stable in neutral solution and only decomposed slowly in alkaline solution. Methylol groups while stable in neutral solution where the molecule is hydrated, are unstable in alkaline solution being hydrolysed to the original urea and formaldehyde. Methylol groups are also more easily hydrolysed than methylene linkages. The value of k for the hydrolysis of monomethylolurea is close to that obtained by Crowe and Lynch<sup>7</sup> and was included

for purposes of comparison. In neutral solution it is seen that formaldehyde will not react with methylenebisethylurea to form monomethylolmethylenebisethylurea owing to hydration of the urea and lack of a strongly nucleophilic nitrogen centre. However, if the monomethylolmethylenebisethylurea be formed separately under more drastic conditions<sup>6</sup> the methylol group is seen to be easily hydrolysed under alkaline conditions, the remaining methylene link being then slowly attacked.

Borzee and Smets<sup>3</sup> have observed that with equimolar concentrated neutral solutions of monomethylolurea and formaldehyde, beyond an initial slow reaction, the course and rate of the reaction is essentially the same as for urea and formaldehyde. This was explained on the basis that the condensation of monomethylolurea itself with formaldehyde comprises the initial slow reaction and that the overall velocity is increased by a more rapid reaction between monomethylolurea and one of the hydrolysis products of this, urea itself. Studies in dilute neutral solution however suggest that hydrolysis of monomethylolurea is negligible and under such conditions it is unlikely that the nucleophilic nitrogen of urea would attack any but an electrophilic centre of monomethylolurea, if such a centre existed. This latter point awaits clarification by further studies of the reactions of methylolureas.

SUMMARY AND CONCLUSIONS.

In an earlier paper<sup>1</sup> the author drew attention to the diversity of products obtained in the urea-formaldehyde reaction and listed factors which influence this reaction. Prior to this, Redfarn<sup>2</sup> had commented on the need for strict control of the reaction, particularly as regards the careful buffering of reaction solutions.

Without attempting to summarize all the papers which have appeared on urea-formaldehyde kinetics, and in this respect it would be more convenient to consult the summaries which accompany the majority of papers, the author intends to outline the more important findings under convenient headings. Where possible the author's work will be treated in greater detail although other related work must necessarily be mentioned in order to obtain a broad view of this field. It should be noted that the greater portion of the kinetic work relates to the initial condensation and only when this is thoroughly understood, will theories of the overall reaction be placed on a secure basis. In view of the number of factors which influence the reaction it is doubtful if recent kinetic studies of the overall reaction<sup>3,4</sup> can be regarded with confidence. The accuracy of kinetic data is limited by the accuracy of analytical methods, even in cases where the reaction is capable of very close control. In addition, analytical methods which may be suitable for following the

1. Smythe, L.E. J. Phys. Colloid Chem., 51, 369 (1947).
2. Redfarn, C.A. British Plastics, 5, 238 (1933).
3. Takahashi, A. Chem. High Polymers (Japan), 7, 115 (1950).
4. Smets, G. and Borzee, A. Jour. Poly. Sci., 8, 371 (1952).

initial condensation under certain carefully controlled conditions, may prove inaccurate when applied to the overall reaction.

#### EXPERIMENTAL METHODS:

The initial condensation of urea and formaldehyde in 1:1 mole ratio to form monomethylolurea, has been studied<sup>1</sup> using hydroxylamine hydrochloride to follow the decrease of free formaldehyde with time. It was shown that monomethylolurea and other condensation products affected the estimation and a correction factor was employed. The accuracy of the method varied from  $\pm 2\%$  for higher concentrations of formaldehyde, to  $\pm 5\%$  in the region of molar solutions. The hydroxylamine hydrochloride method was employed in Parts I and II of this investigation but was not suitable for work with dilute solutions.

Bettelheim and Cedwall<sup>5</sup> employed the Lemme<sup>6</sup> sodium sulphite method, liberated NaOH being determined by titration. It was found that while pure aqueous formaldehyde solutions reacted almost instantaneously with the sulphite, methylolureas influenced the estimation. As a result of experiment it was decided to normalise the sulphite additions and titrations to one minute. It is likely that the accuracy of this method is of the same order as the hydroxylamine hydrochloride method, when applied to reaction solutions containing mono- and dimethylolureas as the principal reaction products.

5. Bettelheim, L. and Cedwall, J. Svensk. Kem. Tid., 60, 208 (1948).

6. Walker, J. "Formaldehyde", p.257, A.C.S. Monograph 98 (1944).

Crowe and Lynch<sup>7</sup> successfully employed the polarographic method for estimating formaldehyde in urea-formaldehyde and general amide-formaldehyde reactions. These authors considered that the general polarographic error was  $\pm 3\%$  of the value determined. Possibly the accuracy was often higher in the case of supporting electrolytes of pH 10.1 - 12.7, since the limiting current is greatly influenced by pH, being greater for alkaline solutions. Later polarographic studies by Smythe<sup>8</sup> in neutral solution where the limiting current is much smaller, indicated an accuracy of  $\pm 5\%$  for the estimation of 0.01 - 0.10 M  $\text{CH}_2\text{O}$  solutions.

De Jong<sup>9</sup> has published a note on the urea-formaldehyde reaction but no details are given of the method used for estimation of formaldehyde.

Takahashi<sup>3</sup> has studied kinetic and other aspects of the urea-formaldehyde reaction but it has not been possible to obtain a full translation of the papers concerned.

Borzee and Smets<sup>4</sup> employed a variety of analytical methods in their urea-formaldehyde studies. While hydroxylamine hydrochloride was used for the estimation of formaldehyde, it was not stated if condensation products interfered. It is therefore not possible to comment on the accuracy of their analytical methods, except in more general terms. It is stated that in the studies, total formaldehyde (uncombined formaldehyde plus methyloleic formaldehyde) was determined by an iodometric

7. Crowe, G.A. and Lynch, C.C. J.A.C.S. 70, 3795 (1948); 71, 3731 (1949); 72, 3622 (1950).
8. Smythe, L.E. See parts III and IV this thesis.
9. De Jong, J.I. Recueil, 69, 1566 (1950).

method or alternatively, by a method using sodium sulphite. The difference between the results of the iodometric and hydroxylamine hydrochloride methods then gave "the variation in concentration of the methylol group." It seems likely that considerable errors have been introduced by employing such methods in kinetic studies. Condensation products, particularly those obtained under acid conditions, would affect the accuracy of both the hydroxylamine hydrochloride and iodometric methods. For example in the iodometric method, it is necessary to dilute the sample to be analysed to a formaldehyde content of 0.2%. Comparatively large volumes of decinormal iodine and 2N NaOH are then added to a 25 ml. aliquot and a ten minute reaction period allowed. It is likely that urea or other condensed products present would affect the accuracy of the method. Investigations have shown<sup>10</sup> that the iodometric method gives accurate results only when applied to pure formaldehyde solutions free from organic compounds (with the exception of methanol and formic acid). The tables of Borzee and Smets record total formaldehyde to four significant figures, the accuracy of estimation of formaldehyde evidently being of the order of  $\pm 0.1\%$  of values recorded. It is extremely doubtful if such a high degree of accuracy is possible in view of what has been said concerning the accuracy of other methods.

It is seen that methods for following the urea formaldehyde reaction kinetically, have been based mainly on the decrease in concentration of formaldehyde during the reaction period.

10. Walker, J. "Formaldehyde", p.260, A.C.S. Monograph 98 (1944).

Other determinations such as melting point and nitrogen content of reaction products, may prove helpful in some cases. Nitrogen content of reaction products however, may not always be representative of pure structural units.

In view of the difficulties mentioned, the author believed that until suitable analytical methods were developed for the estimation of urea, particularly uncombined urea in the presence of reaction products, studies of the reaction employing ratios of reactants other than 1:1, would not prove completely reliable.

Usual methods for the estimation of urea are not applicable in this reaction. The soluble and reactive methyloureas introduce difficulties and reagents such as xanthidrol, which require the use of such drastic condensing agents as glacial acetic acid, are entirely unsuitable. Bettelheim and Cedwall<sup>5</sup> are said to be investigating methods for the estimation of free urea in urea-formaldehyde reaction mixtures but no information is yet available and there are many difficulties to be overcome.

#### PURITY OF COMPOUNDS:

The purity of the compounds used in kinetic studies of the urea-formaldehyde reaction is of considerable importance. For urea, the author has shown that traces of impurities such as ammonium carbonate and ammonium cyanate, have a retarding effect on the reaction. This effect is discussed in Part II of this thesis. Consequently for kinetic studies, urea and substituted ureas must be carefully purified and the solutions prepared immediately prior to use. While evidence has been presented



which indicates that there is an equilibrium between urea, ammonium cyanate and ammonium carbonate in aqueous solution at room temperature, no data are available for similar equilibria in the case of substituted ureas.

De Jong<sup>9</sup> has suggested that ammonium salt impurities in the urea, may be responsible for the initial rapid reaction observed in the case of concentrated solutions. No evidence of this has been detected (see Part II this thesis) but rather has the effect been mainly attributed to the concentration of the reactants in solution. It is suggested that the initial rapid reaction involves anion formation of urea, and dehydration and depolymerization phenomena.

Of the impurities in commercial formalin only two affect the urea-formaldehyde reaction to an appreciable extent. These are formic acid (usually 0.01 - 0.03%) and methanol (usually 5 - 15%). Formic acid does not favour the formation of methylol compounds although the rate of condensation is increased. The formic acid in formalin should be neutralised prior to the kinetic studies, except where suitable buffers are used. The effect of methanol on the reaction rate for 1:1 ratio of reactants has been mentioned in Part II. The author has used methanol free formaldehyde solutions in all other studies. It is well known that methylol derivatives of urea may form ethers<sup>11</sup> with methanol, particularly in the presence of hydrochloric acid. In addition it is probable that hemiacetals are present in alcoholic formaldehyde and even though relatively unstable, their

11. Ritchie, P.D. A Chemistry of Plastics and High Polymers. p.121. Cleaver-Hume, 1949.

existence should be recognised in kinetic studies, unless special precautions are taken to use methanol free solutions.

Criteria of purity of reaction products offer some difficulty. In the case of simple methylolureas and methylenebisureas, melting point and nitrogen determinations are important in the identification of products. Higher temperatures and the use of acid condensing agents lead to ill-defined compounds of indefinite melting point and variable nitrogen content. As mentioned previously, it is also possible that shorter chain hydrated products are present in such mixtures, thereby affecting analytical data.

#### CATALYSTS AND OTHER COMPOUNDS PRESENT IN REACTION MIXTURE:

From the kinetic viewpoint, information is now available in respect of various acids, bases, buffers, ammonium salts, methanol, glycine etc. in both concentrated and dilute solutions. The information is incomplete and further work is required. In acidic medium Borzee and Smets<sup>4</sup> observed a pure acid catalytic effect and draw an analogy with the Mannich<sup>12</sup> reaction. In the experience of the author, no pure acid catalytic effect has been observed and studies have concerned more particularly neutral solutions. In addition, Takahashi<sup>3</sup> observed that the uniformity of the calculated values of  $k$  was best in neutral medium, where the pH of the system did not change through the reaction.

12. Alexander, E. and Underhill, E. J.A.C.S. 71, 4014. (1949).

SOLUTION pH.

Crowe and Lynch<sup>7</sup> have related the urea-formaldehyde reaction rate and the polarographic wave height of formaldehyde to changes of pH and temperature. They consider that with changing pH, both urea and formaldehyde activation equilibria are shifted and the amount of anion of urea is affected more by pH change than by temperature change. The author had examined changes in the pH of unbuffered reaction solutions and suggested that the initial rapid reaction was related to the ionization of urea, in turn dependent upon the hydrogen-ion concentration<sup>1</sup>. Buffering of solutions in the pH range 7.0 - 8.6 showed that for 4 - 8 M solutions, while the initial rapid reaction remained substantially unaltered, dilution increased anion formation of urea in this limited range, more than changing pH.<sup>13</sup> Thus anion formation of urea involves both dilution (with associated hydration) and changing pH. It was suggested in Part I that hydration of urea does not appear to play an important role in the reaction at concentrations of 0.003 - 8 M. While this was found to be the case for more concentrated neutral solutions and for dilute alkaline solutions, studies in dilute neutral solutions indicated hydration of urea. Temperature change is also seen to be less important than the dilution and pH of solutions.

For more concentrated solutions of pH > 5 the effect of depolymerization phenomena is discussed in Part II, where

13. See Parts I and II this thesis.

it is suggested that depolymerization of formaldehyde hydrated polymers, results in the production of cations available for reaction with nucleophilic nitrogen.

On the basis of available evidence it appears that the reaction is capable of close control in neutral and alkaline media<sup>3,7,8,13</sup>. In the case of urea, methylol compounds are formed under such conditions. For dilute solutions of simple N-alkylureas, methylenebisureas are formed in preference to methylol compounds. The effect of pH on the stability of methylenebisureas in dilute solution is discussed in Part IV.

For the urea-formaldehyde reaction, acid conditions appear to favour the formation of methylene compounds and associated cross-linking relatively early in the reaction, although the evidence is somewhat conflicting on this point. The kinetic scheme suggested by Borzee and Smets<sup>4</sup> involves the formation of methylol compounds under acid conditions, in the early as well as the later stages of the reaction. The conflicting claims regarding the nature of products isolated under acid conditions suggest that if methylol compounds are formed, methylene and more highly condensed cross-linked structures are formed very soon thereafter and at the expense of the methylol compounds.

Borzee and Smets<sup>4</sup> only consider the diamide form of urea as taking part in the reaction whereas in this form the nitrogen is deactivated as a nucleophilic centre. In addition the author has pointed out that under acid conditions the distinction between the canonic forms of unionized urea and those derived

from the imidol form would disappear and the N-methylol type of condensation would no longer be favoured<sup>13</sup>. On this evidence the anionic forms of urea are important in the initial condensation.

#### TEMPERATURE:

For temperatures of 20 - 60°C values of  $\Delta E_a$  varied from 14,700 - 15,900 calories. The effect of temperature on the reaction rate for solution pH 6 - 13, for urea and simple N-alkylureas, under a variety of conditions, confirmed that increase in reaction rate with increase in temperature, is not dependent on the kind of amide to any extent. In dilute alkaline solution the effect of temperature change on the amount of anion formation of urea is less than the effect of temperature on the dehydration of methylene glycol<sup>7</sup>.

Borzee and Smets<sup>4</sup> obtained a value of 14,800 calories for  $\Delta E_a$  in the formation of monomethylolurea and this is in agreement, within the limits of experimental error, with 14,700 calories found earlier by the author<sup>1</sup> and 15,900 calories at pH 12.7, by Crowe and Lynch<sup>7</sup>. In neutral medium the later stages of the reaction required 19 - 21 kcal. and for the acidic condensation 8 - 10 kcal.<sup>4</sup> Borzee and Smets<sup>4</sup> explain this variation on the basis that "at higher pH values both the thermal and acid catalytic reactions occur together and the exponent to the hydrogen ion concentration in the expression of the rate of condensation appears to be smaller than unity."

Bettelheim and Cedwall<sup>5</sup> observed that at 40°C for both 1:1 and 1:2 mole ratios the reaction rate passed through a minimum at pH 6.5 and was increased at the 1:2 ratio. No pure catalytic effect was observed and the reaction was not studied at other temperatures.

Under this heading, mention should be made of the exothermic nature of the reaction in the case of relatively concentrated solutions of reactants. The author found it necessary to control the early stages of the reaction when working with 8M - 1M solutions. A rise in temperature of 3 - 5°C occurred in the absence of a cooling coil within the reaction vessel which was in a thermostat bath at 30°C<sup>1</sup>. While the exothermic initial reaction is capable of close control in dilute solutions, concentrated solutions offer some difficulty of control<sup>1</sup>. It would be expected that under acid conditions at temperatures of 55 - 85°C, a vigorous exothermic reaction would dominate the early stages making kinetic studies more difficult. It is well known that industrial condensations of urea and formaldehyde employing acid condensing agents (e.g. formic acid) require cooling to moderate the reaction. This effect has not been mentioned in recent studies.

Work at higher temperatures (50 - 85°C) becomes increasingly difficult owing to loss of formaldehyde during sampling and in cooling samples. The partial pressure of formaldehyde over aqueous solutions is given in the table below:

PARTIAL PRESSURE CH<sub>2</sub>O OVER AQUEOUS SOLUTIONS.

Temp. °C.	CH <sub>2</sub> O conc. gm. CH <sub>2</sub> O/100c.c.	Partial Press. CH <sub>2</sub> m.m. (approx.)
20	40.2	1
45	39.5	3
98-100	39.5	110

For this reason, the author has not found it possible to carry out accurate (kinetic) polarographic studies at temperatures greater than 35°C, although such small losses do not affect the utility of the method for following the course of industrially used condensations.

SOLUTION CONCENTRATION:

The reactivity of both urea and formaldehyde in solution depends largely on environment. Work with 8M solutions suggest that 40 - 50% of the urea existed in an activated form as an anion and this reacted with formaldehyde in the unhydrated form. In Part II the effect of variation in concentration of urea and formaldehyde solutions on the initial reaction may be seen. The dilution of reactants in relation to reaction mechanism was discussed and it was suggested that the reaction of urea and formaldehyde in dilute solution, would be mainly of uniform velocity from zero time. For dilute alkaline solution Crowe and Lynch<sup>7</sup> had found no initial rapid reaction and in addition the reaction was reversible.

The effect of dilution on the reaction of simple N-alkylurea with formaldehyde has been studied. The rate constant

relationship between urea and N-methylurea which was approximately 6 to 1 in the case of 8M solutions was reversed and the reaction with simple N-alkylureas became five times more rapid as compared with urea. The effect of environment, including dilution, on the structure of ureas is discussed in Part III of this thesis and continued in Part IV.

#### UREA: FORMALDEHYDE RATIO.

For reasons mentioned earlier the author's investigations have been primarily concerned with the 1:1 ratio of reactants under a variety of conditions. Earlier work involving different ratios of reactants has been outlined in the introduction to this thesis.

Generally, it appears that with 1:1 ratio of reactants under neutral conditions and low temperatures (5 - 60°C), monomethylolurea is formed by a slow bimolecular reaction. The effect of various conditions on this reaction has been discussed. Further prolonged heating or acidification may result in mixtures of long-chain or branched polymers containing methylene linkages and some lateral methylol groups; while cross-linking is at a minimum. It is suggested that even under such conditions, the reaction products may be contaminated with short open chain structures, unreacted urea and hydrated formaldehyde. A degree of hydration of the urea and lower molecular weight methylol and methylene compounds should not be overlooked.

For the same ratio of reactants with direct acid condensation (pH < 5) the evidence suggests that the formation



of methylolurea is not favoured and methylene structures become more important.

For urea: formaldehyde ratios of 1:2, 1:4 and higher, under neutral conditions, methylol content of the condensation products increases. While one molecule of urea and two of formaldehyde account for the formation of one molecule of dimethylolurea, further heating may result in the formation of methylene linkages and progressive cross-linking with the elimination of some of the lateral methylol groups. Greater amounts of formaldehyde would tend to increase the cross-linking effect. It is possible that with close control of the reaction under neutral conditions further pure compounds or structural units may be identified.

Under acid conditions, with urea: formaldehyde ratios of 1:2, 1:4 and higher, difficulties in the identification of reaction products are encountered. Undoubtedly the degree of cross-linking reaches maximum values under such conditions. Three dimensional cross-linked structures are important and it is probable that even these highly condensed systems contain shorter open chain structures, unreacted formaldehyde and water. Further study under such conditions is required and the whole question is still in sufficient doubt to make further comment superfluous.

Alkaline condensation (e.g. pH 9 - 12) employing urea: formaldehyde ratios of 1:2, 1:4 and greater has not been studied in any detail, probably owing to lack of industrial application for such condensation products. Methylol compounds would constitute important structural units and while some methylene

linkages may be formed, it is likely that hydrolysis of the methylol groups and methylene linkages would also take place. It would appear that cross-linked and three dimensional structures are not important under such conditions.

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In conclusion, it is hoped that kinetic studies of the initial formation of substituted diamides of carbonic acid will contribute to knowledge of the overall reaction. At present it does not appear that a complete kinetic analysis of the urea-formaldehyde reaction is possible, since all variables cannot be measured in any given type of experiment concerning the overall reaction. The generalised picture of condensation polymerizations requires that each successive stage in the polycondensation has the same velocity constant and while considerable experimental evidence has accumulated demonstrating the essential correctness of this in certain reactions, further study of the urea-formaldehyde reaction is required.

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VITA.

Lloyd Earle Smythe was born in Suva, Fiji Islands, on June 15, 1922. He enrolled in the Faculty of Science, University of Sydney, in March, 1940.

In 1942 he was awarded the Timbrol Scholarship in Organic and Applied Chemistry and graduated BACHELOR OF SCIENCE with First Class Honours in Organic and Applied Chemistry in 1943. During the next year he was Research Chemist with Beetle Elliott Plastics Pty. Ltd., Sydney. In 1945, he was appointed Teaching Fellow in Chemistry in the University of Sydney and in 1946 was appointed Lecturer in Chemistry. The degree of MASTER OF SCIENCE was conferred on him in 1946, the thesis presented being entitled: "A Kinetic Study of The Urea-Formaldehyde Reaction".

In 1947 he was appointed Research Chemist, Research and Laboratories Division, Department of Agriculture, Fiji. In 1949 he was appointed Lecturer in Chemistry, University of Tasmania.

He is a member of the Royal Australian Chemical Institute and the Royal Institute of Chemistry of Great Britain and Ireland.

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